

Electrical Conduction and Dielectric Properties of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Ceramics Synthesized by SPS

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Abstract

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramic was synthesized by the spark plasma sintering (SPS) technique. The single-phase composition of CCTO was confirmed by X-ray diffraction. The measurements of the dc electrical conduction and dielectric properties show that the dielectric constant, dielectric loss and leakage current density decrease with the thickness decreasing, meanwhile the variation range of the dielectric constant also narrows greatly in the frequency range between 1 kHz and 1 MHz. In addition, the increase of the nonlinear coefficient for the dc current density–electric field strength curves and the enhanced resistivity both in grain and at grain boundary are also observed. These results can be attributed to the formation of a larger amount of oxygen vacancies near ceramic surface due to the reducing reaction from carbon in the sintering process.

Keywords

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$; Ceramics; Spark Plasma Sintering Technique; Dielectric

Introduction

In recent years, the perovskite-related compound $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has attracted considerable interest due to its extremely high dielectric constant (larger than 10^4), and the dielectric constant shows small temperature dependence near room temperature [1,2], which makes it has potential applications in the field of energy-storage devices. Till now, the mechanism of this giant dielectric response has not been fully understood yet. Since CCTO is unlike some other perovskite compounds, such as CaTiO_3 and BaTiO_3 , no phase transition for the appearance of dipole moment is observed. It is generally considered that the high dielectric constant is not intrinsic but extrinsic and may be related to the material microstructures. Till now, some models have been put forward to explain the origin of the high

dielectric properties, including the internal barrier layer capacitance (IBLC) model [3-7], nanoscale Ca/Cu disorder [8,9], the local displacement for Ti ions [10] and the surface electrode-contact effect [11], etc. Among which, the IBLC model has been widely accepted. In this model, the CCTO ceramic is thought to be composed of the semiconducting grains with a small resistivity and the insulating grain boundaries with a giant resistivity. This grain-boundary-grain composite structure can be reckoned as a complicated equivalent circuit, which consists two parallel elements (resistor and capacitor) connected in series.

According to this model, the giant dielectric constant of CCTO should be related with the difference between the resistivities in grain and at grain boundary. In CCTO ceramic, the grain is thought to be semiconductor due to the formation of conductive Ti^{3+} ions in the heat treatment process. Thus, the content of Ti^{3+} ions in CCTO should make a great impact on the dielectric properties. For example, Li *et al* observed a drastic depression of dielectric constant by doping Mn^{4+} , which is thought to be due to the reduction of the content of Ti^{3+} ion by Mn^{4+} doping [12, 13]. On the other hand, the formation of Ti^{3+} ions in CCTO is often attributed to the formation of oxygen vacancies, and the change on the amount of oxygen vacancies can greatly impact the electronic structure of CCTO, resulting in the change on the electrical properties of the space-charge districts at some interface such as the ceramic surface painted by Ag electrode [14].

The spark plasma sintering (SPS) technology, an appropriate method to prepare density ceramic, has been applied to prepare a variety of materials such as structural ceramics [15], oxide superconductors [16], nano-composites [17], thermoelectric compounds [18],

etc. To the best of our knowledge, the reductive graphite in the SPS sintering process can induce the deoxidization reaction, and result in more Ti^{3+} ions or oxygen vacancies in the prepared CCTO sample. Since in the process of sintering via SPS, the CCTO ceramic is sintered under a large pressure, it is reasonable to think that the content of oxygen vacancies in the inner part of ceramic and near ceramic surface may be different, which may also induce the thickness-related electrical properties. It is noticed that the thickness-dependent electrical properties have been observed in the CCTO ceramics sintered by the conventional solid-state-reaction (SSR) method [7, 19, 20]. Therefore, for the CCTO ceramic sintered by SPS, the related work should also be detailed studied.

Experiments

The CCTO powders were synthesized by the conventional sol-gel method according to Ref 20 and 21, and the final powders were obtained by calcining the precursors at 1035 °C for 24 h.

The CCTO ceramic was then sintered by the SPS technique. In the sintering process, the powders were loaded into a graphite die with the diameter of 15 mm. Graphite foil was placed between the powders and die to avoid possible adhesion. The powders were sintered at 900°C for 5 min under a pressure of 57 MPa. After the sintering, the ceramic was annealed in a muffle furnace at 700°C for 10 h to remove the residual graphite.

The obtained ceramic was then polished (on both sides) to different depth, which changes the thickness of the ceramic from 2.0 mm to 0.7 mm. The qualitative composition analysis at different thickness was performed by X-ray diffraction (XRD, D8-Advanced) with the $\text{CuK}\alpha$ radiation in the 2θ scanning from 20° to 80°. The dielectric and complex impedance spectra were measured by using an impedance analyzer (Agilent 4294), and the dc current density-electric field strength (J - E) measurement was extracted by using an electrometer (Keithley 2182) with the applied voltage from 0 to 40 V. Before the measurement, the air-drying silver conductive paint was brushed on the surfaces of the ceramic and cured at 250°C.

Results and discussion

The XRD patterns for the CCTO ceramic with the thickness of 2.0 and 0.7 mm are shown in Fig. 1. It can be seen that all the XRD peaks can be indexed from

the JCPDS card of CCTO (No.75-2188) and little impure phase is detected. By using the Bragg equation, the lattice constants were determined; and the lattice constants for the CCTO ceramic with the thickness of 2.0 mm and 0.7 mm are 7.381 and 7.383 Å, respectively, close to the standard value in the JCPDS card.

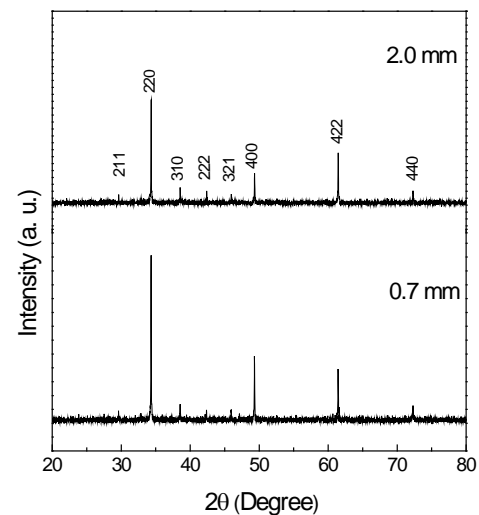


Fig. 1 XRD patterns of CCTO ceramic synthesized by SPS with thickness of 2.0 and 0.7 mm

Even though the XRD results indicate the single-phase composition of CCTO at different thickness in the ceramic, the results of the electrical measurement show clear thickness-dependence. Fig. 2 (a) shows the dc J - E curves for the CCTO ceramic with different thickness. It is shown that with the decrease of thickness, the leakage current densities show monotone reducing, which indicated that samples with larger thickness have more conductive Ti^{3+} ions. Because the formation of these Ti^{3+} ions is related to the deoxidation reaction of Ti^{4+} ions with the reductive carbon in the sintering process, while the concentration of the penetrated carbon should be decreased with the thickness, it is reasonable to think that the content of Ti^{3+} ions should decrease from the sample surface to its internal. On the other hand, considering that the lattice constants just change in the error limit, it is likely that the doped carbons are in the interstitial sites, which means that the content of oxygen vacancies also decreases from the sample surface to its inner part. Furthermore, it is also observed that the J - E curves show clear nonlinear characterization. Generally speaking, the nonlinear characterization of the J - E curve can be analyzed by [22]:

$$J = KE^\alpha, \quad (1)$$

where K is a constant and α is the nonlinear coefficient. Fitting by this equation, the nonlinear coefficient α of different samples was obtained and shown in Fig. 2 (b). It can be seen that, α increases from 1.4 to 2 with the decrease in the thickness of the ceramic. It was noticed that, when the thickness of the sample is less than 1.4 mm, α is close to 2 and changes insignificantly with the thickness decreasing.

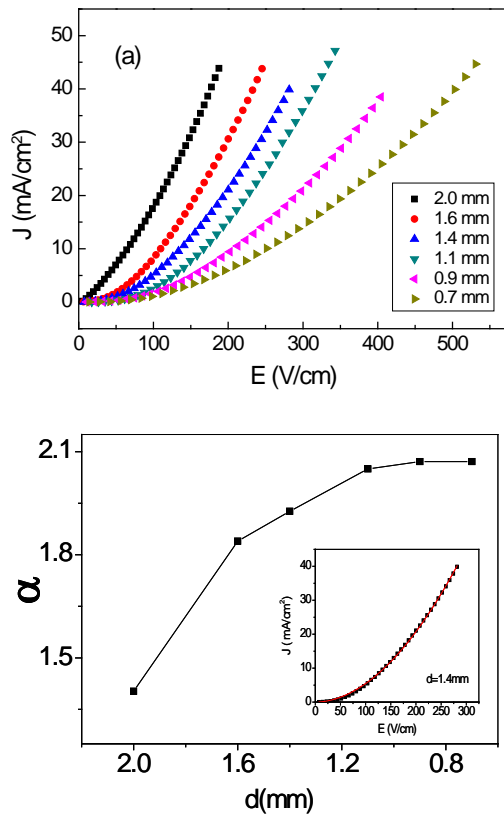
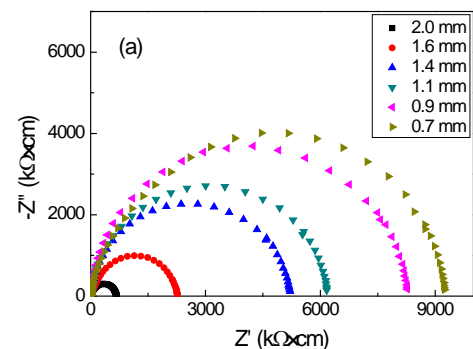


Fig. 2 dc J-E curves (a) and the nonlinear coefficient (b) of CCTO ceramic with different thickness, the inset shows the fitting result for $d = 1.4$ mm

In this work, the oxygen vacancies in CCTO could be divided into two parts: one is generated by the carbon diffusion, whose content should reduce with the decrease of sample thickness; the other originates from the oxygen released in the heating and cooling process of SPS preparation, which is free from change with the thickness. For the ceramic with thickness smaller than 1.4 mm, the oxygen vacancies are formed only from the latter origin, and the electrical conduction behavior could be described by the space-charge-limited current (SCLC) mechanism [23, 24]. According to this mechanism, as the applied field is low, the flowing charges are entrapped near the interface of adjacent districts with large different work function, such as the surface of CCTO ceramic painted by Ag electrode. These entrapped charges form the so-called space charges which have little contribution to electrical conduction [23] until the

field becomes large enough, leading to the nonlinear characterization in the J - E curve [24]. But for the ceramic with thickness larger than 1.4 mm, a larger amount of oxygen vacancies is formed near the ceramic surface due to the reducing reaction from carbon, and the excitation for the charges entrapped near surface is easier under the lower field, and this surface layer with smaller resistivity can be taken as the “transition layer” between electrode and the inner part of ceramic, leading to the decrease in the α values to be between 1 and 2.

The electrical properties can also be depicted by the complex impedance measurement, which is shown in Fig. 3 (a). It can be seen that the complex impedance spectra show clear semi-circle shape, and the diameters of the circles increase greatly with the decrease of thickness. According to the IBL model, this indicates that the difference of the resistivity between the grain and grain boundary increases. Through fitting the impedance spectra by using the circle equation, the grain resistivity was determined by the intercept at the high-frequency limit, and the grain-boundary resistivity equals to the diameter of the circle [22]. Fig. 3 (b) depicts the change of resistivity in grain and at grain boundary with the thickness of the ceramic. It can be seen that both grain resistivity and grain-boundary resistivity increase with the decrease of thickness, that is, the grain resistivity increase from 0.076 k Ω ·cm for the thick sample (2.0 mm) to 0.14 k Ω ·cm for the thin sample (0.7 mm), while the grain-boundary resistivity increase from about 670 k Ω ·cm to about 9300 k Ω ·cm. For comparison, it has been noticed that Adams et al, having reported their results concerning the thickness dependence of resistivity in grain and at grain boundary for the coarse-grained CCTO ceramic sintered by the SSR method, have found totally different results that as the ceramic thickness decreases from 1.9 mm to 0.6 mm, grain-boundary resistivity decreases obviously but the grain resistivity does not show obvious change [7].



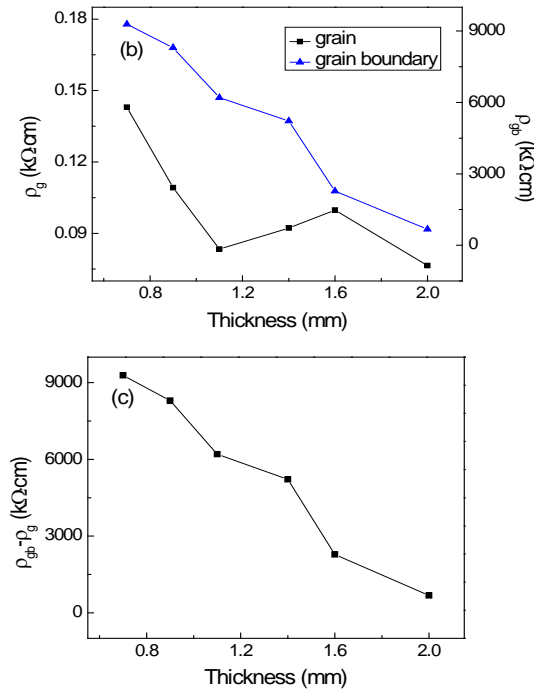


Fig. 3 (a) the complex impedance spectra, (b) the resistivity in grain and at grain boundary, and (c) the difference between the resistivity in grain and at grain boundary for the CCTO ceramic with different thickness

It is known that for the CCTO ceramic, resistivity values at grain boundary and in grain are both closely related with oxygen content. At grain boundary, the absorbed oxygen can capture the flowing electrons in grain, and this charge separation causes a depletion layer and a large grain-boundary resistivity at grain boundary [25,26]. For the CCTO ceramic sintered via SSR, oxygen is enough near ceramic surface, as a result, the grain-boundary resistivity can be larger, but for the CCTO ceramic sintered via SPS, the case is on the contrary, that more carbon is near surface, resulting in the smaller amount of oxygen and smaller grain resistivity near ceramic surface. In grain, the existence of oxygen vacancies can reduce grain resistivity. For the CCTO ceramic sintered via SSR, the oxygen vacancies originate from the oxygen released in the heating process, but for the CCTO ceramic sintered via SPS, additional oxygen vacancies are generated near ceramic surface due to carbon diffusion in the high-pressure sintering process, resulting in the smaller grain resistivity near ceramic surface.

It is clear from Fig. 3 (c), showing the difference between the grain resistivity and the grain-boundary resistivity at different thickness, that the decrease of thickness enlarges such difference, and the enhancement of grain-boundary resistivity clearly plays a critical role. According to the IBL model, the establishment of the grain-boundary depletion layer

may lead to the enhancement of dielectric constant [27]. It is predictable that the dielectric constant may increase with the decrease of thickness. However, as shown in Fig. 4 (a), our result of dielectric measurement is totally on the contrary: The dielectric constant decreases obviously with the decrease of thickness. In addition, it is also noticed that the variation range of the dielectric constant in the measured frequency range (1 kHz~1 MHz) also narrows greatly by the polishing treatment. For example, for the ceramic with the thickness of 2.0 mm, the dielectric constants decrease from about 15000 at 1 kHz to about 5000 at 1 MHz, the variation range reaches 10^4 , while for the ceramic with the thickness of 0.7 mm, the change of dielectric constant between 1 kHz and 1 MHz is only about 600. In addition, it is also noticed that the larger change of dielectric properties in the measured frequency range mainly occurs for the ceramics with the thickness larger than 1.4 mm.

For the ceramics with thicknesses smaller than 1.4 mm, since the existence of space charges has been confirmed, it can be concluded that the besides the common IBL model the space-charge polarization near ceramic surface can also have contribution to the dielectric response. But for the ceramics with larger thicknesses, it is reasonable that the polarization from oxygen vacancies near ceramic surface may have larger contribution to the dielectric constant, especially at low frequency. The similar decrease in dielectric constants by reducing ceramic thickness has also been found in the CCTO ceramic sintered via SSR [19].

Fig. 4 (b) shows the dielectric loss spectra between 1 kHz and 1 MHz. It can be seen that the values of loss for the ceramic with the thickness of 2.0 mm are the largest in the whole frequency range, and at 1 kHz, the loss reaches 0.6. While after polishing, the loss decreases clearly. From the inset figure, it is shown that as the thickness is smaller than 1.4 mm, the loss at 1 kHz is smaller than 0.2. At 1 MHz, the values of loss also show monotone decrease with the decrease of thickness. As far as we know that the low-frequency loss for the electronic ceramic is mainly associated with the thermal effect of leakage current. Thus, the largest low-frequency loss for the ceramic of 2.0 mm clearly indicates the large leakage current, which is consistent with the results of the dc J - E measurement. This also indicates the larger content of conductive Ti^{3+} ions near the surface of the ceramic due to the formed oxygen vacancies.

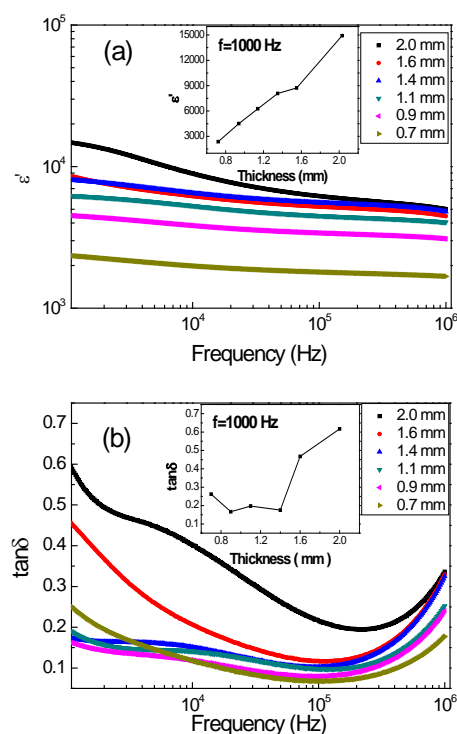


Fig. 4 the dielectric spectra(a) and the loss spectra (b) for the CCTO ceramic with different thickness

Conclusion

Near the surface of the CCTO ceramic synthesized by SPS, a large amount of oxygen vacancies forms due to the reduction reactions in the sintering process. This is confirmed by the large leakage current density and the smaller nonlinear coefficient of the dc J - E curves. These surface oxygen vacancies introduce the large low-frequency dielectric constants and dielectric loss, and the small resistivity in grain and at grain boundary.

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